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We demonstrate the process of low-pressure organic vapor-phase deposition (LP-OVPD) for the growth of crystalline thin films of the organic charge-transfer salt 4'-dimethylamino-N-methyl-4-stilbazolium tosylate (DAST) on amorphous TiO_2 substrates. LP-OVPD grown films exhibit polycrystallinity with long-range structural ordering limited only by substrate size. Film surface coverage and macroscopic ordering are strongly determined by the preparation of the TiO_2 surface prior to growth. The morphology and ordering of the films are also found to depend on the deposition temperature and the composition of the precursor molecules. These results suggest that LP-OVPD films are of sufficient quality for use in optical waveguide and related photonic devices.

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Macroscopically Ordered Thin Films of an Organic Salt Grown by Low Pressure Organic Vapor Phase Deposition

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Abstract

We demonstrate the process of low-pressure organic vapor-phase deposition (LP-OVPD) for the growth of crystalline thin films of the organic charge-transfer salt 4'-dimethylamino-N-methyl-4-stilbazolium tosylate (DAST) on amorphous TiO_2 substrates. LP-OVPD grown films exhibit polycrystallinity with long-range structural ordering limited only by substrate size. Film surface coverage and macroscopic ordering are strongly determined by the preparation of the TiO_2 surface prior to growth. The morphology and ordering of the films are also found to depend on the deposition temperature and the composition of the precursor molecules. These results suggest that LP-OVPD films are of sufficient quality for use in optical waveguide and related photonic devices.

Introduction

There is considerable interest in new organic materials with large second-order hyperpolarizabilities, β, for use in nonlinear optical (NLO) devices such as frequency converters and electro-optic (EO) modulators. In particular, molecular organic salts can exhibit a very large β due to their non-centrosymmetric crystal structure.[1] Such crystalline materials can be more stable than polymers which require electric-field poling to attain spatial asymmetry and the ensuing NLO properties.[2] The crystalline organometallic charge-transfer salt, 4'-dimethylamino-N-methyl-4-stilbazolium tosylate (DAST), is a

particularly interesting material for NLO device applications due to its large EO coefficient and a low dielectric constant, giving rise to a high modulator figure of merit.[2]

It is desirable to grow optical quality thin films of DAST and other organic salts for integrated opto-electronic devices. Previous attempts to deposit DAST by heating in vacuum were unsuccessful, resulting in molecular decomposition prior to evaporation.[3,4] Furthermore, the highly incongruent vapor pressures of the DAST neutral precursors 4'-dimethylamino-4-stilbazole (DAS) and methyl-tosylate (MT), which result in uncontrollably rapid evaporation of MT and nonstoichiometric growth, render double-source co-evaporation in vacuum unfeasible.

In addition to difficulties incurred from incongruent vapor pressures of the precursors, organic salts are bonded by a combination of van der Waals (vdW) and Coulomb forces. Since Coulomb interactions are long range compared to the induced dipole interaction of vdW bonded solids (the latter decaying as $1/R^6$, where R is the intermolecular spacing), crystalline disorder induced by film-substrate interactions can propagate over large distances. For this reason, it is very difficult to initiate macroscopically ordered growth between an organic salt and a substrate to which there is no commensurate, or epitaxial relationship. Unfortunately, such epitaxial relationships are rare for molecular organic thin films grown on inorganic substrates, severely constraining the range of materials combinations which can be grown in an ordered fashion. Furthermore, the growth of the salt occurs by reacting neutral precursors to form the resulting anion-cation pair. Hence, vacuum deposition of such complex and strongly bonded solids has, to date, not lead to the growth of thin film organic salts with the macroscopic order needed in most practical device applications.

To avoid problems inherent in vacuum deposition of the neutral precursors, a new growth technique known as organic vapor phase deposition (OVPD)[4,5] was introduced which led to the stoichiometric growth of polar, multiple-component compounds such as DAST. In this method, vapor transported precursors of DAS and MT combine on a substrate in the heated zone of a hot wall reactor to form thin polycrystalline DAST films. In contrast to vacuum deposition, OVPD was carried out in a reactor held at atmospheric pressure. Films grown on Au substrates exhibited ordering over only a few millimeters. Unfortunately, reproducible macroscopic ordering was not obtainable using that technique. One of the primary disadvantages of atmospheric pressure OVPD is that film growth is diffusion limited. This is in contrast to vacuum deposition where growth is kinetically limited, i.e. where the growth rate is controlled by the rate of arrival of the constituent precursors at the substrate surface. Hence, film disorder and compositional inhomogenuities in OVPD are strongly influenced by the details of the flow patterns and kinetics of the carrier gases within the reactor tube.

To address the problems inherent in atmospheric pressure growth, while taking advantage of the ability of OVPD to produce stoichiometric films of organic salts, we introduce here a significant modification of the OVPD process where the reactor vessel pressure is reduced into the 10-100 Torr range. At these pressures, kinetically rather than diffusion controlled growth dominates. This new process, called low-pressure OVPD (LP-OVPD)6, has been use to demonstrate the growth of DAST thin films with long-range ordering limited, at times, only by substrate size (extending to several centimeters, in our experiments). The extent of the film order is examined via the azimuthal dependence of

the relative second-harmonic generation (SHG) efficiency, together with polarized optical microscopy. X-ray diffraction measurements indicate that the films consist of the SHG-active crystalline phase of DAST belonging to the monoclinic Cc space group, with the [001] crystal axis oriented normal to the substrate plane.[1,7] Such long-range crystalline order is a prerequisite for realizing high-performance, low-loss NLO devices such as waveguide modulators.

Growth

As previously reported,[5] the growth reactor was a 5 cm diameter glass tube, placed in a three-zone horizontal furnace, as shown in Fig. 1. Oriented polycrystalline DAST films were obtained at substrate temperatures between 200 C and 215 C, at deposition pressures of 50 Torr to 75 Torr. Either DAS or DASI powder sources were used with the crucible at 210 +/- 6 C and 243 +/- 6 C, respectively, while the MT bubbler temperature was kept at 110 - 125 C using an oil bath. Nitrogen was used to purge the main chamber and to provide a carrier for the MT. The flow rates were 50 sccm and 200 sccm for the purge and carrier gases, respectively.

The DAST films were grown on thermally oxidized Si (111) wafers (nominally 1.3 um thick SiO2) coated with a 3200Å thick film of TiO_2. The miscut angle between the surface normal and the Si (111) plane was nominally 3 +/- 0.5 degrees. Prior to deposition, the substrates were cleaned by rinsing in boiling detergent followed by a rinse in boiling isopropanol and drying in pure nitrogen. For one set of substrates, the TiO_2 films were exposed to a $CF_4:O_2$ (in proportion of 45:5) plasma at RF powers ranging from 50W to 150W. A second set of substrates were exposed to a solution of 4:1 $H_2SO_4:H_2O$ at an initial temperature of 80 C for 15 minutes, and then rinsed in water. After cleaning, the substrates were placed in the reaction zone of the furnace at an angle of either 30 or 45 degrees to the gas-flow direction. While heating the chamber, the TiO_2 substrates were exposed to hot DAS vapor for 30 min. After temperature stabilization, the MT was introduced into the reactor for a 50 min long growth.

LP-OVPD Grown DAST Films

a. Structure

These growth conditions result in the deposition of polycrystalline films of DAST ranging in thickness from 2um to >5um. Optical micrographs of a DAST film viewed under polarized light and exhibiting several crystalline domains are shown in Fig. 2. Such films were grown from a DAS precursor at a temperature of 213 C. Figure 2(a) shows a film grown at a deposition pressure of 50 Torr on a clean TiO2 coated Si (111) substrate. The typical domain size as determined using a polarized-light microscope is $5mm^2$-$20mm^2$, with adjacent domains apparently oriented randomly with respect to each other and the substrate. The growth mode is dendritic, with an estimated surface coverage of ~50%.

Subjecting the TiO_2 substrates to various treatments prior to deposition has a significant effect on the surface coverage and crystallite alignment of the films. Figure 2(b) shows a film grown at a deposition pressure of 75 Torr on a TiO_2 substrate which was first exposed to 4:1 $H_2SO_4:H_2O$ as described above. The surface coverage is ~80%, with island areas between $10^2 um^2$ and $10^4 um^2$. The crystal domain size, as estimated from polarized-
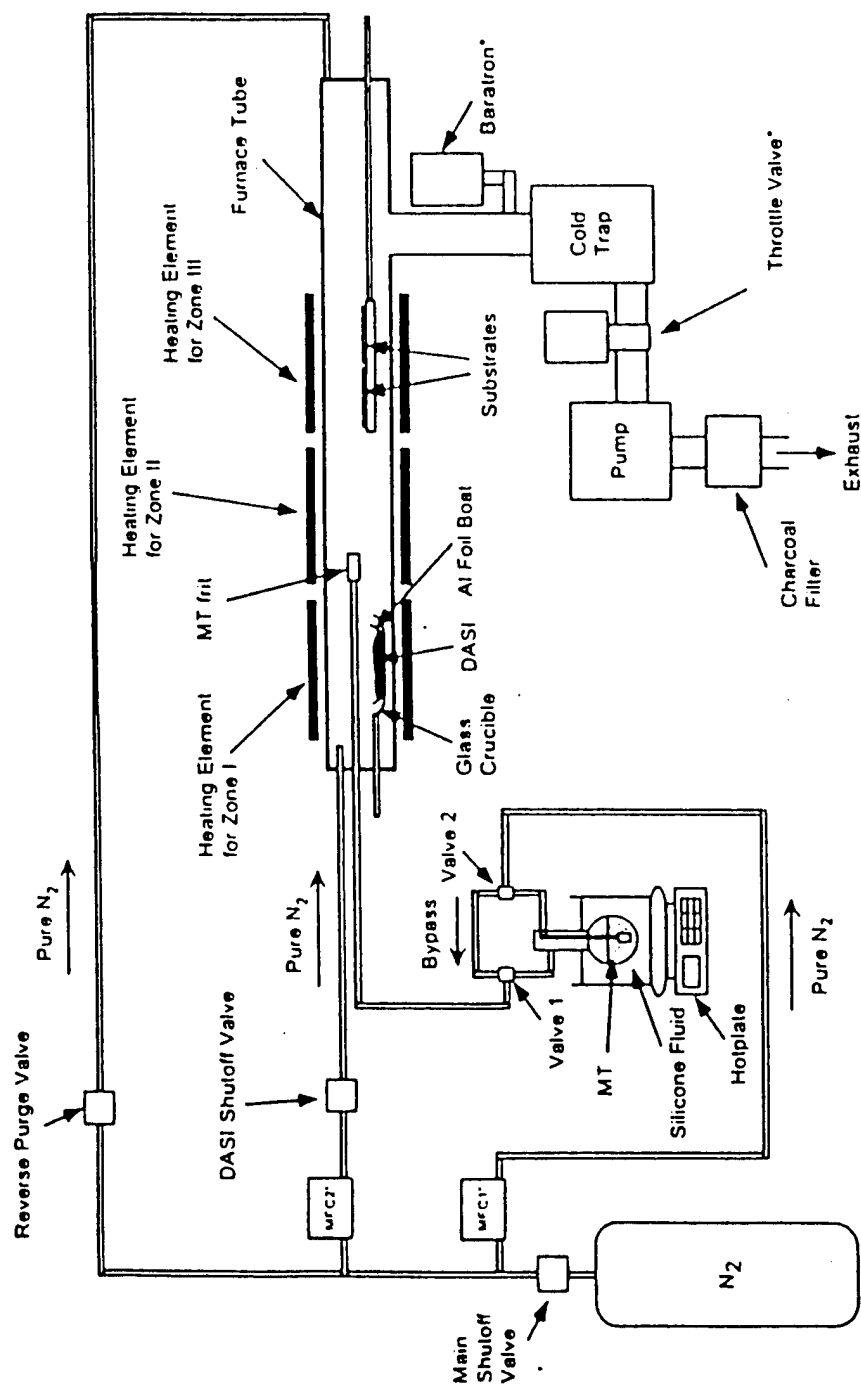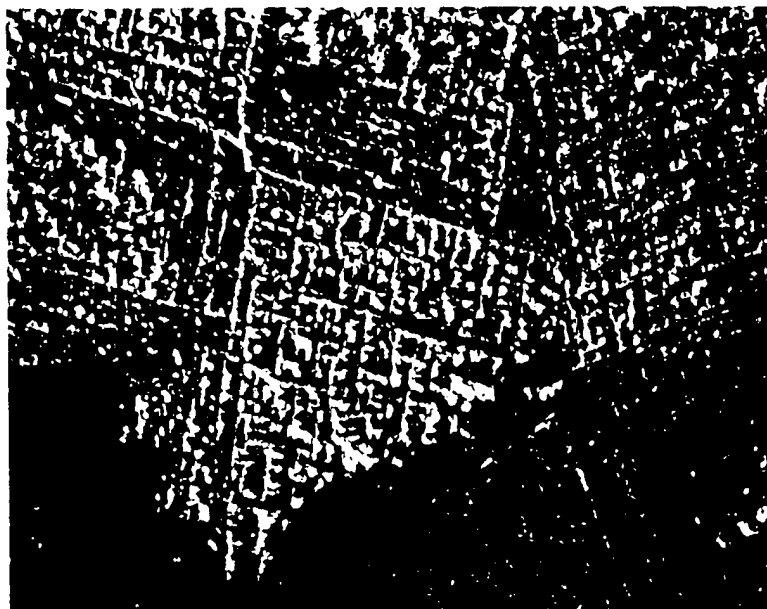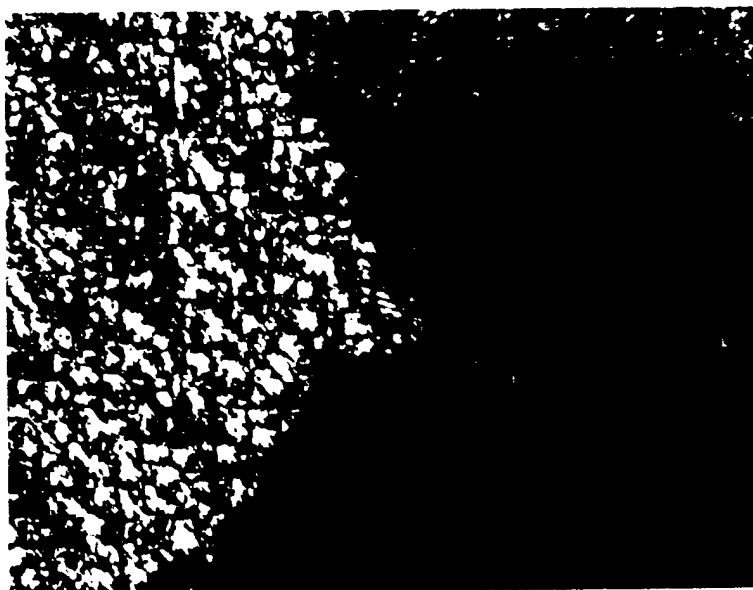
Fig1. Schematic representation of the LP-OVPD reactor used to grow DAST films.

200μm

200μm

Fig. 2(a)   Polarized-light micrograph of a DAS-initiated DAST film grown on TiO$_2$ at a temperature of 213 C. The growth is dendritic.

Fig. 2(b)   Polarized-light micrograph of a DAST film grown under conditions similar to (a) on H$_2$SO$_4$-treated TiO$_2$. Different domains appear as regions of different color.

light microscopy is >100mm². A magnified view of a film is shown in Fig. 3(a), where parallel fissures relieve strain between the film and substrate. Figure 3(b) is an atomic-force microscope (AFM) image of one of these fissures. The accretion of material near the edge of the fissure confirms that these features are formed during growth, and are not the outcome of differential contraction of the film and substrate due to cooling at the end of the growth cycle. This is further established by the presence of terraces running parallel to the fissures, as shown in Fig. 3(c).

X-ray diffraction was employed to further ascertain the crystalline structure of the LP-OVPD grown films. The samples were exposed to the collimated CuKα radiation [λ=1.54 Angstrom] from a rotating anode and were aligned with the momentum transfer, Q=4πsin(2θ/2)/λ where 2θ is the scattering angle, parallel to the substrate surface normal [Bragg Brentano geometry]. The resolution [full-width at half-maximum] of the instrument for the momentum transfer ΔQ was approximatelly 0.0007 Å. Figure 4(a) shows the diffracred intensity asa function of Q, obtained for a thin film of DAST on a TiO2 coated SiO2/Si substrate. The bare substrate is also shown to highlight the DAST reflection peaks. A distinct set of peaks clearly resolved at Q = 0.7036±0.0002Å-1, 1.4082±0.0001Å^{-1}, 2.1130±0.0002Å^{-1} and 2.8177±0.001Å^{-1} are tentatively assigned to the (00n), n=2,4,6,8 reflections of the monoclinic (a=10.365Å, b=11.322Å, c=17.893 Å, β=92.24°)[7], SHG-active DAST crystal structure. From these data the lattice spacing is determined to be 17.83+/-0.01Å, in agreement with 17.70+/-0.15Å previously obtained far a DAST film grown on glass[4]. The lack of additional peaks in the diffraction pattern signifies that the monoclinic crystalline form of DAST is predominant. Assuming that the reflections are broadened by the finite crystallite size, using the Scherrer formula[8] we obtain a domain size of approximately 920Å after deconvolving the instrumental line width from the (004) reflection peak width.

Figure 4(b) shows the x-ray rocking curve also measured for the (004) reflection. Here, the angle ω between the surface and the incident x-ray wave vector has been transformed into the in-plane component of the momentum transfer using Q=2π[cos(2θ-ω)-cos(ω)]/λ. Since the peak above the diffuse background scattering is centered at Q= 0Å^{-1}, and assuming the previous peak assignment, DAST is found to grow preferentially oriented with the (a,b)-plane of the unit cell parallel to the film surface. Furthermore, the single peak in the ω-scan indicates that, to within the detection limit, other preferred growth directions of DAST with respect to the substrate normal do not exist. Since the largest dipole moment of DAST lies in the (a,b)-plane, this orientation of the unit cell is preferable for in-plane waveguide modulators where the applied electric field is parallel to the substrate surface.

Thin films of DAST were also successfully grown from a DASI precursor. In general, such films appear rougher and thicker than DAS-initiated films. Figure 5(a) shows a film grown using a DASI precursor at 200 C. The typical domain size for TiO$_2$ substrates not exposed to chemical treatment prior to growth is between 10mm² and 30mm². The non-uniform thickness of the film is evident in the scanning electron micrograph of a smaller region of the film shown in Fig. 5(b), suggesting the dominance of a Stranski-Krastonov (layer-plus-island) growth mode. The surface coverage of such films is estimated to be between 50% and 70%. Increasing the deposition temperature to
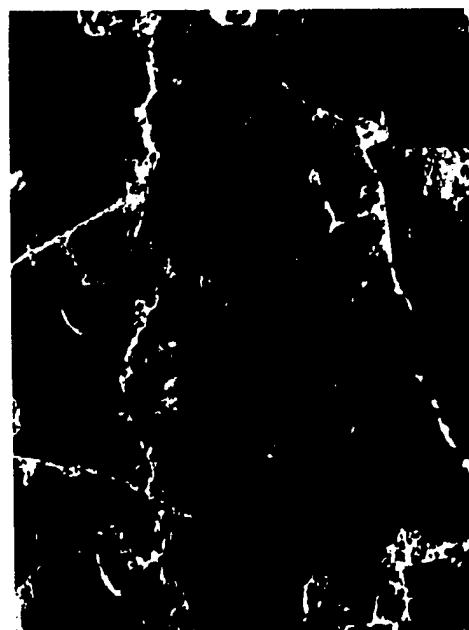
6

b

100μm
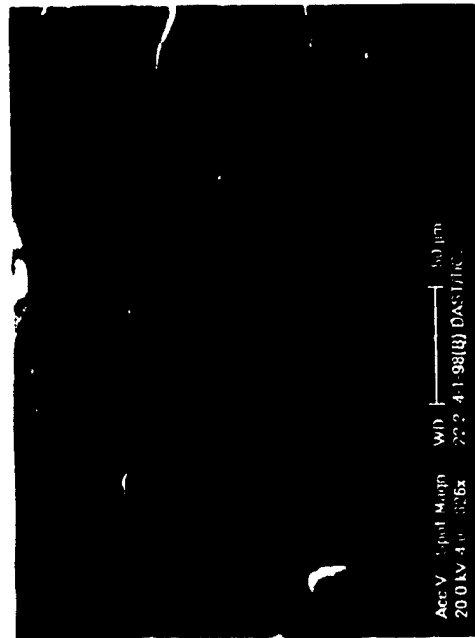
c

1mm

Fig. 3(a)   Optical micrograph of a DAST crystallite exhibiting parallel strain-relief fissures.

Fig. 3(b)   Atomic force microscope image of a DAST strain relief defect.

Fig. 3(c)   Scanning electron micrograph of a DAST film, showing parallel terraces initiated by accretion at the edges of the fissures. Here, a layer-by-layer growth mode is clearly apparent.
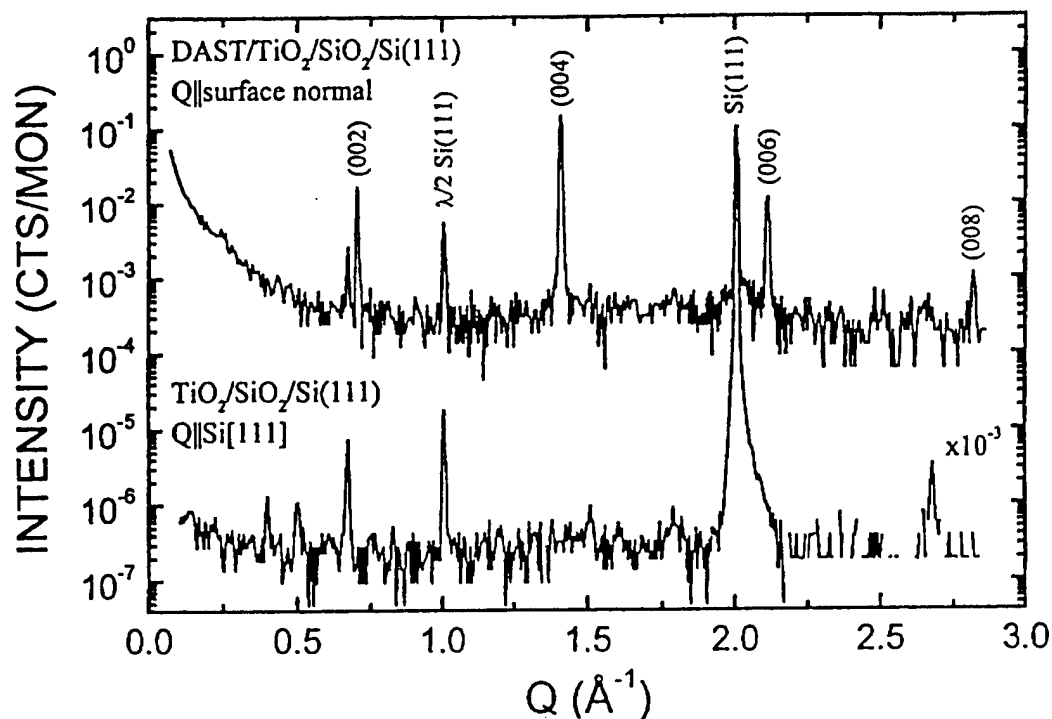
Fig. 4(a)   Comparison between the diffraction patterns from a TiO_2-coated SiO_2/Si substrate, and a similar substrate with a deposited thin film of DAST. The substrate diffraction intensity has been divided by 10^3 for clarity. Tentative assignments have been given to reflections of DAST based on the monoclinic crystal structure.
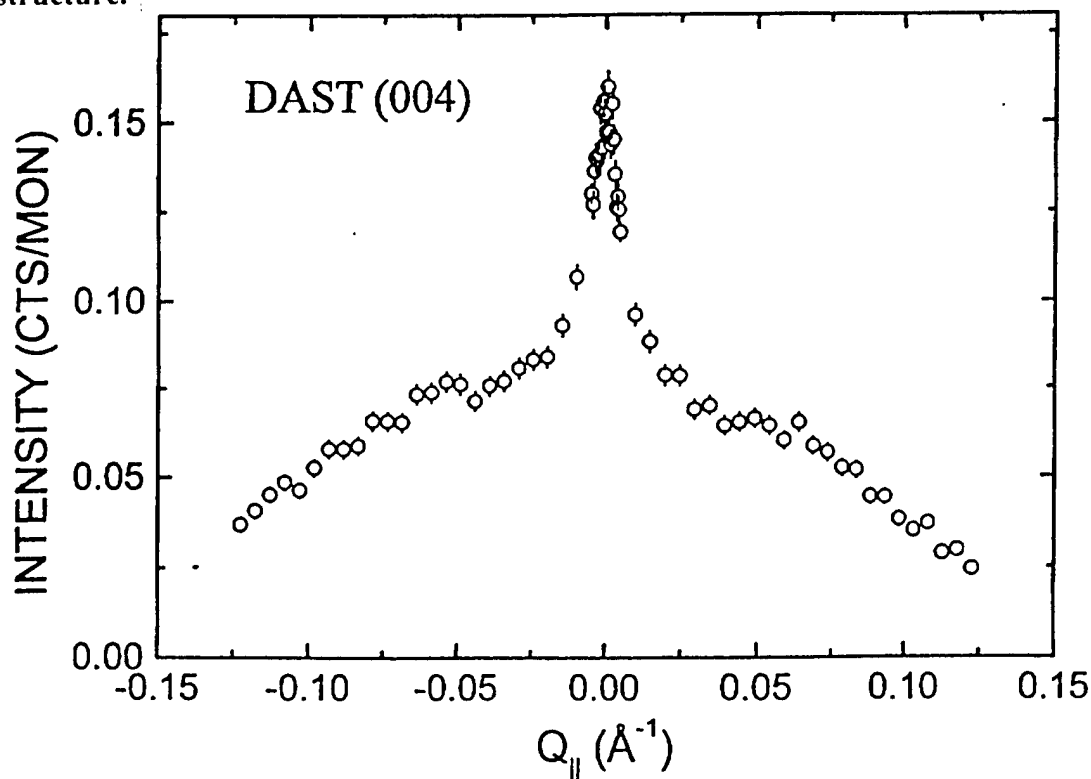

Fig. 4(b)   Rocking curve measured for the (004) DAST reflection. The rocking angle is transformed into the in-plane component of the moment transfer ($Q\|$). The peak position at $Q = 0\text{Å}^{-1}$ indicates that the DAST (a,b)-plane is oriented parallel to the substrate surface.

213 C results in a more uniform thickness, with >80% surface coverage. Figure 5(c) shows a typical DAST film deposited on 4:1 H_2SO_4:H2O-treated TiO_2, at a temperature of 213 C. The surface coverage is increased to ~100% over the scale shown in the figure, and also the island size has dramatically increased. The film appears bright green in reflection, with a rough surface. The domain size, as estimated from polarized-light microscopy, is >100mm2, with some samples exhibiting a single domain aligned across the entire 20mm x 10mm substrate.

b. Optical Properties

The macroscopic azimuthal ordering of the DAST films was examined by observing the SHG intensity using a polarized Nd:YAG laser fundamental pump beam at a wavelength λ =1.06 um with a collimated spot size of ~80 mm^2. The samples were mounted on a rotating plate whose axis was collinear with the laser beam, and rotated about the azimuth with respect to the input-beam polarization. Figure 6 shows the SHG signal at λ=0.53 um generated from a DAST film grown on a 4:1 H_2SO_4:H_2O-treated TiO_2 substrate. The macroscopic in-plane ordering of the film is evident from the high contrast between the maximum and minimum signals across the wafer surface as the sample is rotated 90° in the polarized beam. We note that the high contrast ratio and angular dependence observed in Fig. 6 were not present in all samples, indicating that the crystallinity and long-range ordering depend strongly on the growth temperature.

A more precise optical study of the crystalline ordering of films grown at 200 C was carried out by measuring the azimuthal dependence of the second harmonic signal generated from a fundamental pump beam of λ=1.9 um with a ~300 um2 area, as described previously.[5] A polar plot of the SHG intensity is shown in Fig. 7, together with the expected $\sin^4 \phi$ dependence. The symmetry in the location of the maxima and minima together with the pronounced angular dependence of the SHG signal reaffirm the presence of macroscopic in-plane crystalline ordering.

Discussion

The observed ordered (or quasi-epitaxial) growth[9] of DAST on the various TiO_2 substrates indicates the presence of significant intermolecular and molecule-substrate interactions, leading to macroscopic alignment of polycrystallites nucleated at widely separated sites across the substrate surface. The surface must therefore provide some form of template which results in a preferred film orientation. The molecule-substrate interactions are in part determined by the ionic nature of TiO_2[10] which results in strong binding of the polar DAST molecules. In contrast, it has been observed that when DAST is grown on covalently bonded SiO_2 substrates, the film fails to wet the surface.[4] Previous[4] and also recent attempts to grow DAST on Au resulted in crystallite dimensions of <50 um, indicating that the choice of substrate is crucial for achieving long range order. Furthermore, exposing the substrate to DAS vapor prior to the introduction of MT may result in the nucleation of a thin "template" layer, further facilitating DAST adhesion to the substrate.

AFM scans of both treated and as-grown TiO_2 films show the lack of significant changes in surface roughness or morphology for H_2SO_4-treated substrates, suggesting that the improvement in the DAST film quality is due primarily to alterations in surface

9

chemistry. One possible reaction may be protonation of the TiO_2 surface during acid-exposure, thus creating a strongly interacting surface-dipole layer[11] which promotes the adhesion of DAST to the substrate.

We observe that the macroscopic crystalline alignment was improved for films grown on TiO_2 predeposited onto thermally oxidized vicinal Si(111) surfaces. It is known that the surface of Si(11n) substrates is characterized by single-layer and double-layer stepped surfaces.[12] This preexisting array of steps results in a long-range periodic undulation in the surface potential which may also account for the highly ordered growth of DAST. Nevertheless, we note that there is no direct evidence that the stepped surface structure is conserved after thermal oxidation of the Si surface. Alternatively, the TiO_2 film may induce strain in the wafer. The presence of such strain may result in bowing of the wafer surface, thereby generating an electrostatic strain field leading to ordered growth. While either strain or step induced templating may lead to the observed macroscopic crystalline alignment, there is as yet no direct evidence for their existence.

As a step towards realizing a practical EO modulator, DAST was also deposited on 5 um wide by 1000Å – 3000Å thick rib-waveguides pre-patterned onto the TiO_2 coated substrates. It was verified by polarized light microscopy that the DAST crystallites grow preferentially along the waveguide length, with some crystals several millimeters long. This again implies that step-discontinuities or other corrugations on the substrate surface such as those provided by the rib waveguide edges, may significantly enhance nucleation and long-range ordering of DAST films on otherwise amorphous substrates. This has previously been observed in the preferential alignment of small-molecular-weight thin films along waveguide rib-edges achieved via vacuum deposition.[13]

Summary

In conclusion, we have demonstrated the new process of low pressure organic vapor-phase deposition to grow thin films of the organic salt DAST on amorphous TiO_2-coated Si substrates. X-ray diffraction and optical analysis confirm that the LP-OVPD thin films consist of the SHG-active, monoclinic crystalline phase of DAST. Under appropriate growth conditions and surface treatments, the films exhibit high surface-coverage and long-range structural ordering, with some crystals extending across the entire 2 cm wafer surface. Variations in the substrate surface assist in nucleation and alignment of the DAST molecules, thus greatly improving film quality. It is clear that LP-OVPD, which is carried out in the kinetically limited growth regime, results in significant improvements in the macroscopic ordering of the Coulombically bonded organic salts as compared with earlier growths using the diffusion-limited, atmospheric pressure OVPD technique. The long-range ordering and crystallinity observed in films of DAST grown on TiO_2 waveguides may be adequate for demonstrating a wide range of optically active devices.

b

200nm

100nm

1 2 3 4 μm

a

50μm

c
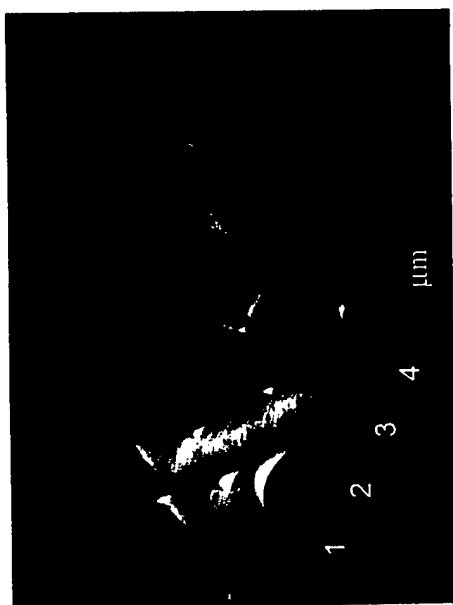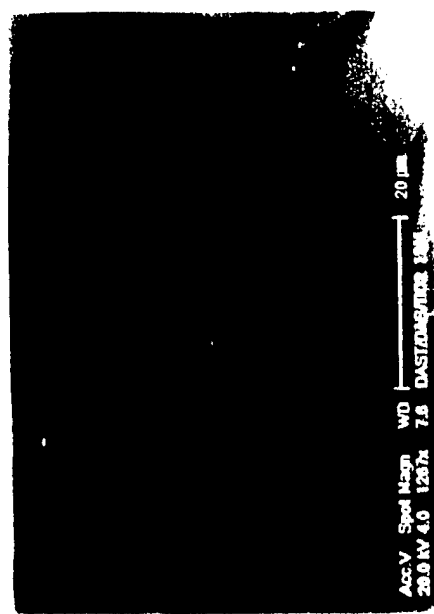
Fig. 5(a)   Optical micrograph using polarized light of a DAST film grown at a temperature of 200C.
Fig. 5(b)   Scanning electron micrograph of a magnified region of (a).
Fig. 5(c)   Optical micrograph of an aligned DAST film grown on H_2SO_4-treated TiO$_2$-coated SiO$_2$/Si (111) substrate at a temperature of 213C.
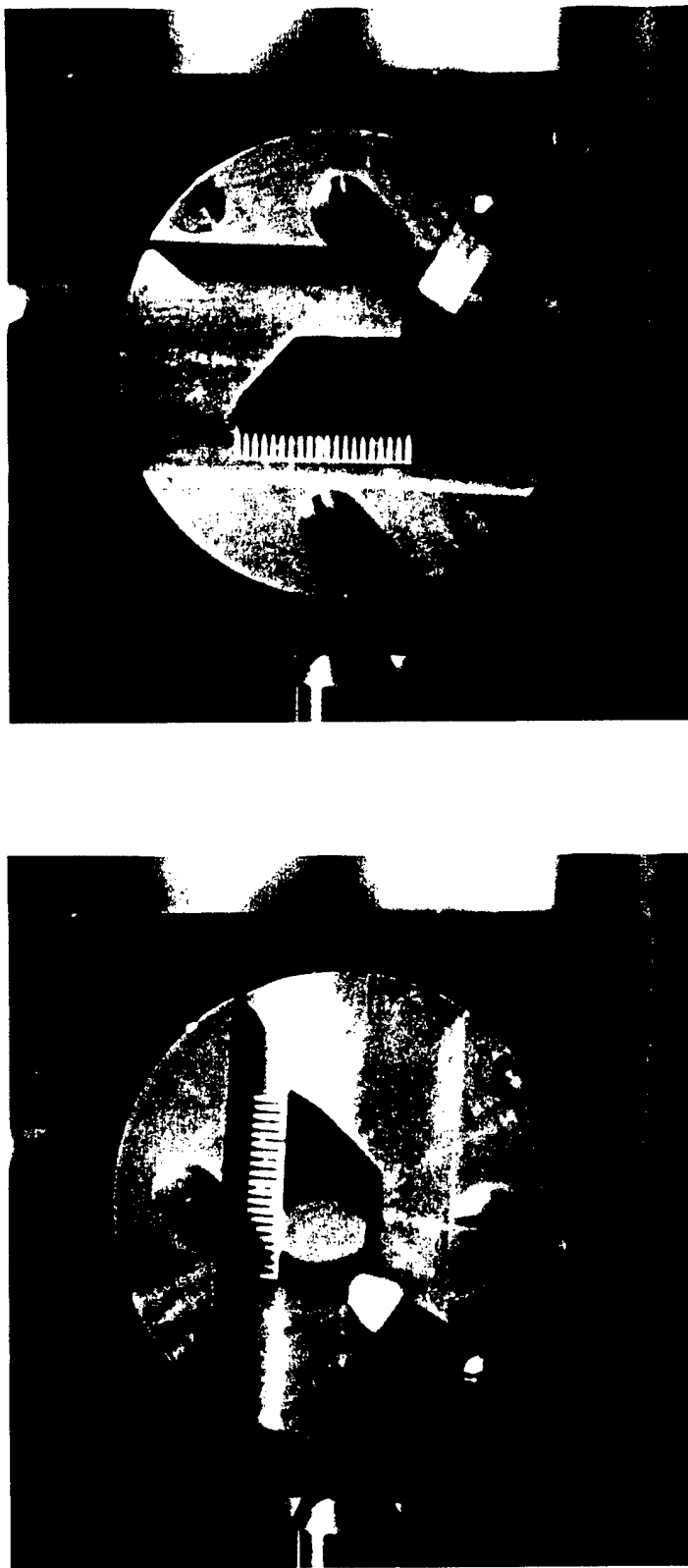
Fig. 6 The 0.53 um second harmonic signal of a 5 um thick DAST film at two different orientations with respect to the 1.06 um wavelength pump laser polarization. The complete extinction of the SHG signal in the upper panel suggests ordering of the film across the entire wafer surface. Scale gradations are in millimeters.
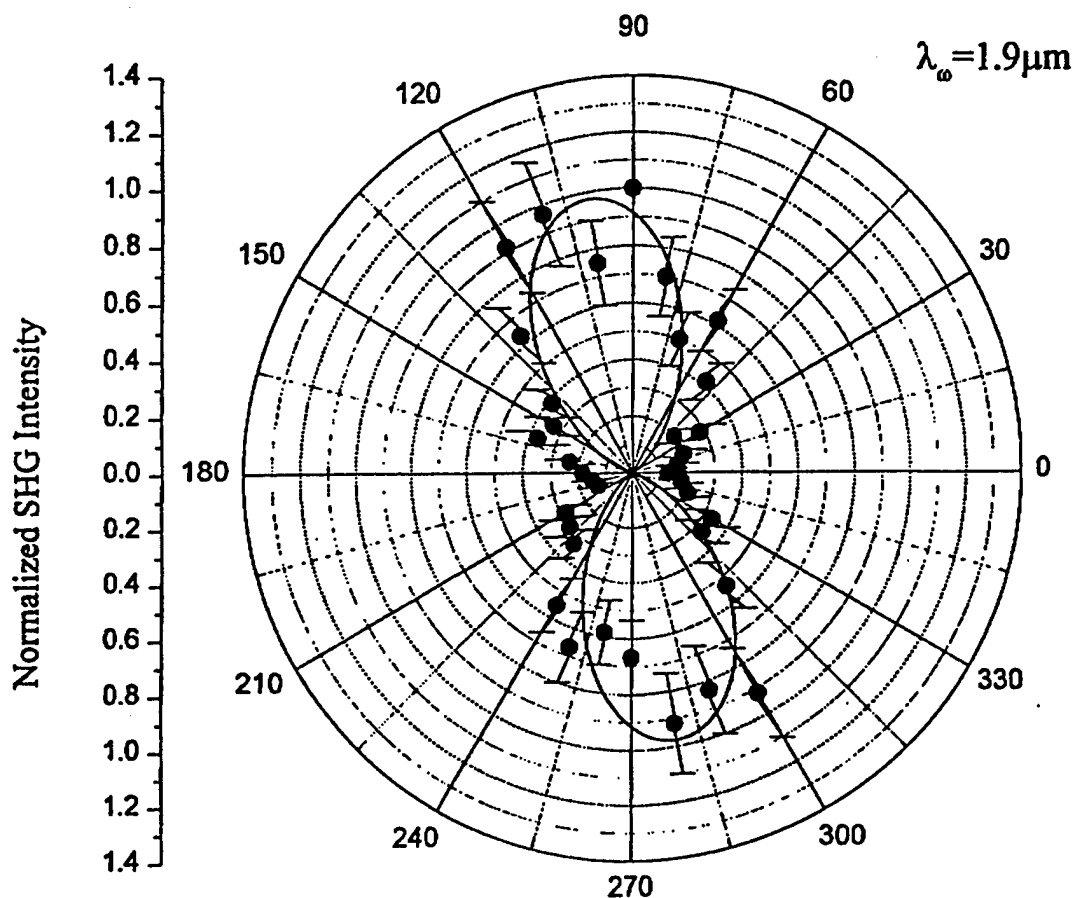
Fig. 7 Polarization dependence of the second harmonic generation efficiency of the DAST film grown on H_2SO_4:H_2O-treated TiO_2 on SiO_2/Si (111) substrates . The maximum intensity is observed when the polarization of the beam is aligned along the substrate edge, as shown in Fig. 6, bottom panel. The solid curve is $\sin^4 \phi$, where ω is the azimuth angle.

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